Metal Complexes with an Imino Nitroxyl Diradical

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IN DEDICATION TO THE LATE PROFESSOR OLIVIER KAHN FOR HIS PIONEERING CONTRIBUTIONS TO THE FIELD OF MOLECULAR MAGNETISM

Copper(II), nickel(II), and zinc(II) complexes with tridentate imino nitroxyl diradicals were prepared and their magnetic properties were studied. The copper(II) and nickel(II) complexes showed substantial ferromagnetic interactions being operative between metal centers and coordinated radical ligands. © 2001

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INTRODUCTION

There has been increasing interest in molecule-based magnetic materials, in which the combination of metal ions and organic radicals was often used to construct assembled systems. The magnetic interaction between metal ions and organic radicals is either ferromagnetic or antiferromagnetic and this depends on the nature of each magnetic orbital and coordination atmosphere. For example, Cu^{2+} or Ni^{2+} ions having only $d\sigma$ spins are, in general, likely to show the ferromagnetic interactions with π-radicals (1), while a metal ion with $d\pi$ spins favors the antiferromagnetic interaction with π-radicals (2). In this article we present new metal complexes with a diradical of imino nitroxide (bisimpy) (Scheme 1), [CuCl(bisimpy)(MeOH)](PF$_6$) (**1**), [NiCl(bisimpy) (H$_2$O)$_2$]Cl·2H$_2$O (**2**), and [ZnCl$_2$(bisimpy)] (**3**), which show ferromagnetic interactions between paramagnetic metal ions and a coordinated ligand. Theoretical calculations on diradical, zinc(II), and copper(II) complexes were also performed to study the spin density change on radical ligands before and after coordination to the metal ions.

EXPERIMENTAL

Syntheses

The imino nitroxyl diradical of bisimpy was prepared by the method reported in (3). Reactions of hydrated metal chloride with bisimpy in methanol yielded the corresponding complexes, [CuCl(bisimpy)(MeOH)] (PF$_6$) (**1**), [NiCl (bisimpy)(H$_2$O)$_2$]Cl·2H$_2$O (**2**), and [ZnCl$_2$(bisimpy)] (**3**). Elemental analyses of the compounds are as follows: for **1**: Anal. Calcd for C$_{20}$H$_{31}$ClCuF$_6$N$_5$O$_3$P: C, 37.92; H, 4.93; N, 11.06%. Found: C, 37.82; H, 4.91; N, 10.96%. For **2**: Anal. Calcd for C$_{19}$H$_{35}$Cl$_2$N$_5$NiO$_6$: C, 40.81; H, 6.31; N, 12.53%. Found: C, 40.80; H, 6.25; N, 12.55%. For **3**: Anal. Calcd for C$_{19}$H$_{27}$Cl$_2$N$_5$O$_2$Zn: C, 46.20; H, 5.51; N, 14.18%. Found: C, 46.29; H, 5.39; N, 14.00%.

Magnetic Measurements

Magnetic susceptibility data were collected in the temperature range of 2.0 to 300 K and in an applied field of 5 kG on a Quantum Design model MPMS SQUID magnetometer. Pascal's constants were used to determine the diamagnetic corrections (4). The X-band EPR spectra of frozen ethanol solutions were recorded at various temperatures between 5.0 and 80 K with a Bruker spectrometer (ESP-300E), which was equipped with a helium continuous-flow cryostat, a Hall probe, and a frequency meter.

RESULTS AND DISCUSSIONS

Structures

[CuCl(bisimpy)(MeOH)](PF$_6$) (**1**). Complex **1** crystallizes in the orthorhombic space group $Cmc2_1$ and the complex molecule is positioned on the mirror plane (Fig. 1). Coordination geometry about the Cu(II) ion is a square pyramid, of which equatorial sites are occupied by a chloride ion and three nitrogen atoms from bisimpy, and methanol coordinates to the Cu(II) ion from the apical position. The Cu–N2 (imino nitroxide) bond is slightly longer (2.069(2) Å) than the Cu–N1 (pyridine) (1.979(2) Å), and the Cu–Cl bond length is 2.2226(7) Å. The coordination bond lengths with the equatorial atoms are shorter than that with
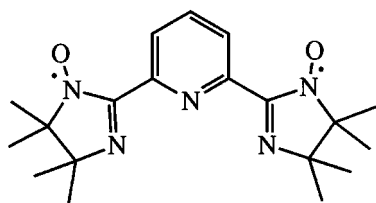
SCHEME 1.

the apical oxygen atoms (Cu–O2S = 2.261(2)). The Cu(II) ion lies at a mean distance of 0.203(1) Å above the equatorial coordination plane (Cl–N2–N1–N2′). The noncoordinated dinitronyl and imino nitroxides bridged by phenyl, thiophenyl, or 2,2′-bithienyl groups, the aromatic rings and imino or nitronyl nitroxyl planes tilt toward each other with about 30° (5). Upon coordination to the metal ion of the diradical ligand, the imino nitroxyl fragments and the pyridine plane in bisimpy become coplanar with the dihedral angles of 2.6(2)°.

$[NiCl(bisimpy)(H_2O)_2]Cl \cdot 2H_2O$ (**2**). Complex **2** crystallizes in the triclinic space group $P\bar{1}$ (Fig. 2). In **2**, the Ni(II) ion has a distorted octahedral coordination geometry of which equatorial coordination sites were occupied by three nitrogen (bisimpy) and oxygen (H_2O) atoms, and a chloride ion and an oxygen (H_2O) atom coordinated to the Ni(II) ion from the axial positions. The bond length of Ni(1)–Cl(1) is 2.3870(8) Å; the other coordination bond lengths are in the range of 2.033(2)–2.148(2) Å.

$[ZnCl_2(bisimpy)]$ (**3**). Complex **3** crystallizes in the monoclinic space group $P2_1/n$ (Fig. 3a). In **3**, there are two crystallographically independent molecules, which stack to form a dimeric unit (Fig. 3b). Coordination geometry about the Zn(II) ions in the two molecules is trigonal bipyramidal with similar coordination geometry. Equatorial positions are occupied by two chloride ions and a pyridyl nitrogen

atom from bisimpy. The Zn–Cl and Zn–N(pyridine) bond lengths are 2.2266(8)–2.2436(7) Å and 2.155(2)–2.147(2) Å, respectively, and the equatorial bond angles about the Zn(II) ions are in the range of 115.52(5)°–112.78(3)° for Zn1 and 115.98(5)°–125.42(3)° for Zn2. Imino nitrogen atoms of the radicals coordinate to the Zn(II) ions from the apical positions with bond lengths of 2.264(2)–2.298(2) Å. The imino nitroxyl and pyridyl planes of the bisimpy in **2** are almost coplanar to each other, of which dihedral angles are less than 5.7°.

Magnetic Properties

Magnetic susceptibility measurements for **1–3** were performed in the temperature range of 2.0–300 K.

$[ZnCl_2(bisimpy)]$ (**3**). The $\chi_m T$ value at 300 K for **3** is 0.785 emu mol^{-1} K, which corresponds to the value expected for the uncorrelated two spin system (Fig. 4). The $\chi_m T$ values steadily decreased as the temperature was lowered, which means the substantial antiferromagnetic interaction is operative in the high-temperature region.

In the organic multiradical compounds, the spin polarization mechanism is useful for predicting the sign of the magnetic interaction between radical centers. The radical ligand bisimpy has two imino nitroxyl groups linked at the meta position of the pyridine group, which fulfils the condition for the occurrence of intraligand ferromagnetic interaction. The observed magnetic interaction for **3** was antiferromagnetic; there must be, therefore, an antiferromagnetic pathway that overcomes the intraligand ferromagnetic interaction. In **3** the two complex molecules stack to form a dimeric structure with parallel arrangements, and the close interradical (O···O or N···O) distances of 3.535(3)–3.760(3) Å were observed (Fig. 3b). This situation

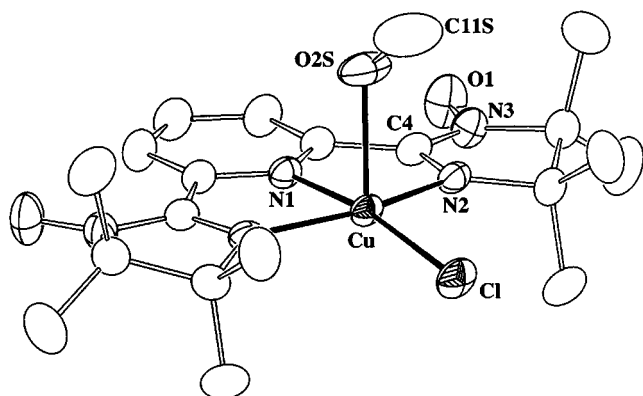**FIG. 1.** Ortep drawing of the cationic part of [CuCl(bisimpy)(MeOH)] (PF$_6$) (**1**). Selected bond lengths (Å) are Cu–N(1), 1.979(2); Cu–N(2), 2.0686(15); Cu–Cl, 2.2226(7); and Cu–O(2S), 2.261(2).
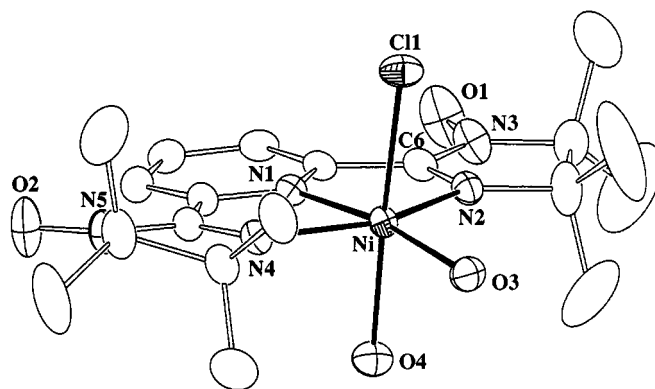

FIG. 2. Ortep drawing of the [NiCl(bisimpy)(H$_2$O)$_2$]$^+$ part of **2**. Selected bond lengths (Å) are Ni(1)–O(3), 2.033(2); Ni(1)–N(1), 2.040(2); Ni(1)–O(4), 2.106(2); Ni(1)–N(4), 2.126(2); Ni(1)–N(2), 2.148(2); and Ni(1)–Cl(1), 2.3870(8).
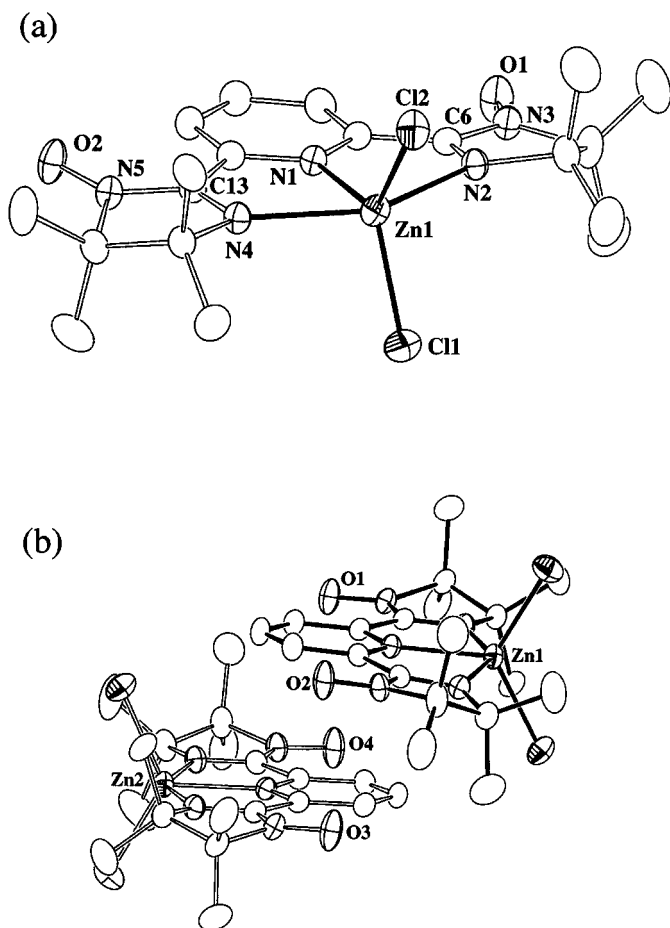
(a)

(b)

FIG. 3. Ortep drawing of (a) [ZnCl$_2$(bisimpy)] (**3**) and (b) dimeric structure. Selected bond lengths (Å) are Zn(1)–N(1), 2.1548(18); Zn(1)–Cl(2), 2.2266(8); Zn(1)–Cl(1), 2.2436(7); Zn(1)–N(4), 2.2636(17); Zn(1)–N(2), 2.2885(17); and Zn(2)–N(6), 2.1466(18).

FIG. 4. $\chi_m T$–T plot of [ZnCl$_2$(bisimpy)] (**3**). The solid line corresponds to the theoretical curve, the parameters of which are given in the text.

Hatfield and co-workers (7). Exchange coupling constants J_1 and J_2 represent intra- and interligand magnetic interactions, respectively. In the calculation, the intraligand J_1 and g values were fixed to $+6.5\,\text{cm}^{-1}$ and 2.0, respectively. A least-square calculation yielded the J_2 value of $-18.4\,\text{cm}^{-1}$.

[CuCl(*bisimpy*)(*MeOH*)](*PF*$_6$) (**1**). In **1**, the Cu(II) ion has an unpaired electron on the $d_{x^2-y^2}$ orbital and the ligand bisimpy coordinating from the equatorial positions has two radical moieties. The $\chi_m T$ value at 300 K was 1.60 emu mol^{-1} K, which is higher than the value (1.125 emu mol^{-1} K) expected for the uncorrelated three-spin system (Fig. 6).

The $\chi_m T$ values increased as the temperature was lowered and reached the plateau value (1.89 emu mol^{-1} K) at 40 K.

favors the intradimer magnetic interaction being antiferromagnetic. X-band EPR spectra of the frozen ethanol solution for **3** were measured to exclude the effect of the intermolecular magnetic interactions. The EPR spectrum, which consists of intense signals at 0.33–0.35 T and a well-resolved half-field signal at 0.16 T, shows typical triplet signals with the axial symmetry. The Curie plot of the EPR signal intensity in the temperature range of 6–72 K gave a positive θ value of 2.4 K, and this proves the intramolecular magnetic interaction being ferromagnetic (see Fig. 5).

The temperature variations of the EPR intensity data were used to estimate the intramolecular ferromagnetic interaction by using the modified Bleaney–Bowers equation ($H = -2JS_1 \cdot S_2$) (6), and the J value of $+6.5\,\text{cm}^{-1}$ was obtained. In the dimeric unit of **3**, there are four imino nitroxyl groups with intramolecular ferromagnetic and intermolecular antiferromagnetic interactions. The magnetic data of **3** was analyzed by the four-spin model derived by
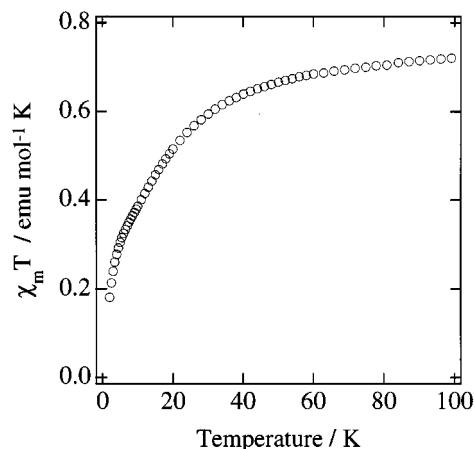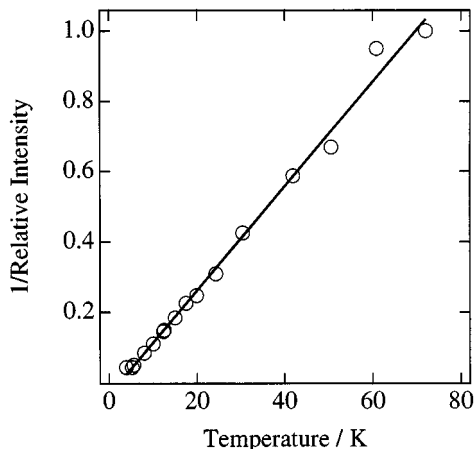

FIG. 5. Curie plots of the EPR signal intensity ($\Delta m_s = 2$ transition) of [ZnCl$_2$(bisimpy)] (**3**).
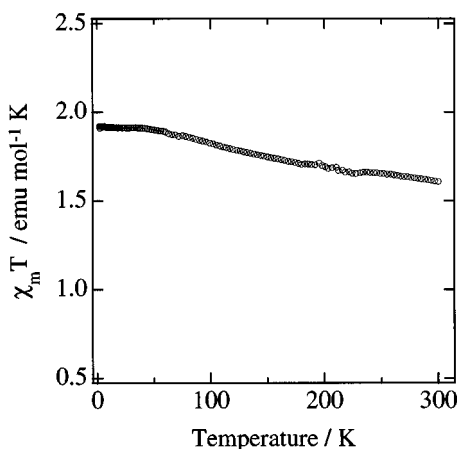
FIG. 6. $\chi_m T$–T plot of [CuCl(bisimpy)(MeOH)](PF$_6$) (**1**).
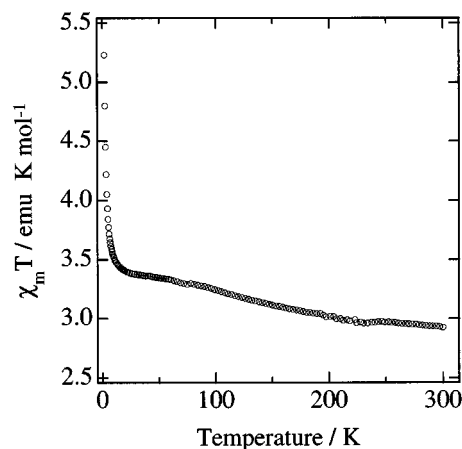
FIG. 7. $\chi_m T$–T plot of [NiCl(bisimpy)(H$_2$O)$_2$]Cl·2H$_2$O (**2**).

The Curie constant for the $S = \frac{3}{2}$ state is 1.876 emu K mol^{-1} with $g = 2.0$; it is, therefore, concluded that the three half-spins in **1** have a parallel alignment below 40 K. The ferromagnetic interaction between the Cu(II) ion and radical moieties is due to the orthogonality of the $d_{x^2-y^2}$ and $p\pi$ orbitals, and the intraligand ferromagnetic interaction is also expected by the spin polarization mechanism. Two exchange parameters J_1 and J_2 for the Cu(II)–radical and intraligand magnetic interactions were introduced for the analysis of the magnetic data. The spin Hamiltonian has the form of $H = -2J_1(2S_{Cu} \cdot S_{radical}) - 2J_2S_{radical} \cdot S_{radical}$. When the two imino nitroxides in bisimpy are weakly coupled as in **3**, the exchange coupling constant J_1 was estimated to be $+165(1)$ cm^{-1} with the g_{Cu} value of 2.017(1), where the J_2 and $g_{radical}$ values were fixed to $+6.5$ cm^{-1} and 2.0, respectively. The estimated coupling constants were in good agreement with the results of molecular orbital calculations with the DFT method, which will be discussed in the following section.

[*NiCl(bisimpy)(H$_2$O)$_2$]Cl·2H$_2$O* (**2**). The room temperature $\chi_m T$ value for **2** showed gradual increase to the plateau value of 3.33 emu mol^{-1} K at 56 K, followed by a sudden increase at 16 K. The observed magnetic behavior reveals the relatively strong intramolecular ferromagnetic interactions being propagated with the weak intermolecular ferromagnetic interaction (Fig. 7).

The magnetic data were analyzed by a three-spin model that has J_1 and J_2 representing exchange parameters of Ni(II)–radical and radical–radical interactions, respectively. The theoretical expression of the magnetic susceptibility was derived by Kambe's method (8). The least-square calculation gave the best fit parameters of g_{Ni} and J_1 being 2.169(3) and $+120(2)$ cm^{-1}, respectively, where J_2 (interradical interaction) and $g_{radical}$ were fixed to be $+6.5$ cm^{-1}

and 2.00, respectively, and the intermolecular ferromagnetic interaction was estimated to be $\theta = +0.8$ K.

DFT Calculations

DFT calculations for the free ligand bisimpy (abbreviated as **L**), [CuCl(bisimpy)(MeOH)](PF$_6$) (**1**), and [ZnCl$_2$(bisimpy)] (**2**) were performed using Gaussian 98 (9). The Becke3LYP hybrid functional was used throughout this work. The LANL2DZ basis functions and effective core potentials for Cu and Zn developed by Hay and Wadt (10) and 6-31G* basis functions for C, H, N, and O atoms were used in every calculations (11). Geometry of the compounds was taken from the X-ray analyses and geometry optimizations were not performed, and the methyl groups in the imino nitroxides were replaced with hydrogen atoms. The spin density of radical ligands **L**, **1**, and **2** is localized mainly on the imino nitroxyl groups. Strong positive spin populations are found on the iminyl nitrogen and nitroxide group, and negative spin populations are observed on the bridging sp^2 carbon atom. In metal complexes the magnetic interactions between the coordinated imino nitroxides are mediated by the metal ion and the pyridine group. In **2** the interradical magnetic interaction is very weak and the DFT results for **2** showed negligibly small spin delocalization on the Zn^{2+}. Magnetic interactions are propagated via charge transfer interaction between paramagnetic centers and between a paramagnetic center and a bridging atom (12, 13). The weak interradical magnetic interactions in **2** is due to a very high-energy charge transfer state between the Zn(II) ion and an imino nitroxyl group. On the other hand, the spin populations on the pyridyl groups in **L**, **1**, and **2** were not substantial either, although positive and negative spins are alternately aligned in the pyridine groups. The spin polarization mechanism is not an effective description for the diradical ligand studied, and this was understandable

due to the relatively small negative spin density on the bridging sp^2 carbon atom.

CONCLUSION

The Cu(II) complex with the diradical ligands has the spin quartet ground state, and a fairly strong ferromagnetic interaction is operative due to the orthogonality of the Cu(II)-$d\sigma$ and imino nitroxide $p\pi$ orbitals. It was concluded that the spin population of the diradical ligand in this system changed by only a small amount upon coordination to the metal ions.

ACKNOWLEDGMENT

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